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厦门大学

博　士　学　位　论　文

θ溶液中星形聚合物刷以及二元混合聚合物刷的分子动力学研究

Molecular Dynamics Study of Starlike Polymer Brushes in θ-Solvent and Mixed Binary Brushes

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摘要

聚合物刷通常指的是紧密排列吸附在基面上的聚合物层，在功能性涂层、生物材料或胶质等方面有着重要应用，因此受到很多关注和研究。在过去的研究中，线性聚合物刷已经得到了深入全面的研究。近年来的研究热点逐渐转向具有更加复杂结构的聚合物刷，比如多分叉聚合物刷或是混合聚合物刷。这样复杂体系受到关注的原因有很多：多分叉聚合物刷具有更多的末端单体可以进行功能修饰，因此可以用来制成快速响应的智能表面涂层以及润滑涂层、防污涂层；更重要的是，多分叉聚合物刷体系广泛地存在于生物体系中；对于混合聚合物刷来说，有着单一组分的聚合物刷所不具备的特性，它们在化学开关方面有着更广泛的前景。

本文通过分子动力学模拟研究了在θ溶液中星形聚合物刷以及更为复杂的由线性和星形聚合物组成的二元混合聚合物刷的动力学行为。第1-3章主要介绍了关于聚合物、聚合物刷的研究背景和相关理论。

第四章研究了θ溶液中星形聚合物刷的分子动力学行为。星形聚合物作为最简单的树枝状聚合物，对于了解多分叉聚合物有着重要意义。在我们的研究中，首先通过分子动力学模拟得到θ 溶液中星形聚合物刷的高度和平均密度，发现Alexander-de Gennes 标度理论和分子动力学模拟结果出现了偏差，不再适用于θ 溶液的情况。接着，我们根据Merlitz 等人针对θ 溶液中的线性聚合物刷所提出的简单的Flory Huggins 平均场模型，考虑了$ln(1-c)$泰勒展开式中的更高阶项，将这个简单的Flory Huggins 平均场应用到星形聚合物刷中去，成功解释了Alexander-de Gennes 标度理论不适用于θ溶液中的星形聚合物刷的原因，研究发现平均场理论分析得到的结果和分子动力学模拟结果吻合得很好。为了研究不同溶液给聚合物带来的影响，我们将良溶液和θ 溶液中的星形聚合物刷进行了对比。在接枝面密度足够大时，处于不同溶液中的刷子内部的星形聚合物都会产生两种完全不同的状态：完全拉伸和完全坍塌。但是在θ 溶液中，直到接枝面密度σ 达到0.1 时，才出现这样的双组分结构，而良溶液中的星形聚合物刷在接枝面密度$\sigma = 0.02$ 时已出现这样的双组分结构，并且这样双组分结构不是静止的，而是保持动态平衡。我们统计了聚合物链在不同状态间的翻转频率，发现在良溶液中，聚合物在不同状态之间的转变频率更高，这是由于聚合物在良溶液中能够更好地膨胀拉伸开来。而在θ 溶液中，单体之间的相互作用力不仅存在排斥力，还有吸引力，这将导致在相同接枝面密度情况下，在θ 溶液中聚合物刷有着更高的单体密度，容易造成聚合物纠缠在一起，并且增大了聚合物翻转时的摩擦力。

第五章研究了更为复杂的二元混合聚合物刷在良性溶液和不良溶液中的结构、表面性质和动力学行为。二元混合聚合物刷由化学性质相同但结构不同的线性链和4

个分叉的星形聚合物组成。我们研究了线性链长、接枝面密度、温度对混合聚合物刷的影响，并与自洽场理论的分析结果进行对比[1, 2]。在对不同组分的末端单体分布和单体密度分布的分析中，发现线性链在二元混合聚合物刷表现得很活跃，只需要稍微增加线性链长就使得大部分线性链的状态从坍塌转变成拉伸。增加线性链长还会对聚合物刷的结构有着戏剧性的影响，也就是线性链和星形聚合物在刷子内部的位置相互对调。有趣的是，在线性链长适中时，改变接枝面密度可以带来如增加线性链一样的效果：低密度时，线性链回缩至聚合物刷底部，而星形聚合物在聚合物刷的上层占主导地位，随着密度的增加，一部分线性链从聚合物刷表面挤出，在高密度区间时，绝大多数线性链伸展到聚合物刷的表面。我们将以上讨论结果总结在相图中。接着将不同线性链长、接枝面密度的二元混合聚合物刷置于溶液性质变化的环境中，通过降低温度，实现了溶液从良性溶液到不良溶液的转变。在线性链长适中时，降低温度使得聚合物刷的表面构成物从线性链和星形聚合物的末端单体混合体转变成为单一的星形聚合物。这一发现也许还不足以实现智能转换的化学“开关”，但给予我们一个启示：只需要稍微改变不同组分的化学性质，使其对溶液具有不同的选择性，这样就能够实现随着外界环境变化而快速反应的智能涂层。

最后一章节概述和总结了博士期间的工作，以及对未来研究工作的展望。

关键词：θ溶液，星形聚合物刷，混合聚合物刷，分子动力学，平均场理论

Abstract

Densely grafted polymer layers, commonly known as polymer brushes, have been studied and received ample attention in recent years because of their important applications in technical coatings, biomaterials or colloid stabilization. As the properties of brushes made of linear chains have been thoroughly studied in the past several years, recently more and more attention is being paid on more complex systems, e.g. branched polymer brushes or mixed polymer brushes. These systems are interesting for a couple of reasons: Since branched polymers are offering an enhanced number of end groups which could be functionalized, they are regarded good candidates for stimuli-responsive surface layers. They are further expected to offer improved lubricant and anti-fouling properties. Most importantly, branched polymer brushes are known to play vital roles in biological materials. Compared with pure polymer brushes, mixed brushes have unique properties that make they to be perfect candidates of switchable layers.

Molecular dynamics simulations were performed to study the properties of starlike polymer brushes in θ-solvent and mixed polymer brushes made by linear and starlike polymers. The background and theories regarding polymer and polymer brushes are introduced in Chapter 1,2,3.

In Chapter 4, Starlike polymer could be considered as the simplest dendrimer, which is of great importance to understand the properties of dendrimer. In our study, the height and average concentration of starlike polymer brushes in θ-solvent are calculated, indicating that Alexander-de Gennes scaling theory is invalid for starlike polymer brushes in θ-solvent neither. Further on, for star polymer brushes, we implemented a simple Flory-Huggins type mean-field model that was proposed by Merlitz et.al for linear brushes in θ-solvent. It explains the deviation from molecular dynamics simulations, resulting from ignoring the higher order terms of Taylor expansion of $ln(1-c)$. In order to figure out how the solvent quality affects properties of polymer brushes, simulation results of starlike polymer brushes in good solvent and θ-solvent are compared. First of all, both of them show a dual-population structure (completely stretched and collapsed) of polymer inside brushes when the grafting density is sufficiently large. The difference lies in that in θ-solvent it requires a higher grafting density (0.1 for θ-solvent, 0.02 for good solvent) until two-population structure appears. It is shown that molecules inside a starlike brush can switch between completely stretched and collapsed states. The conformation of starlike polymer is not static, but rather in dynamics equilibrium. The fliprates of brushes in different solvent qualities are calculated. It shows a higher frequency in good solvent. The reason is that the macromolecules easily stretch in good solvent compared with θ-solvent. The interaction between two beads in θ-solvent contains not only repulsive part, but also attractive part, indicating that polymer brushes

in θ-solvent collapsed easily. As a consequence, brushes in θ-solvent have higher average concentration, which induces the entanglement of polymers and stronger friction of flipping between stretched and collapsed states.

In Chapter 5, we also investigate the structural, surface and dynamic properties of binary polymer brushes in good solvent and poor solvent, composed of functional 4-arm star polymers and chemically identical linear polymers of different molecular weights. The dependency of linear chain length, grafting density and temperature on the structure of brush are investigated and compared with recent self-consistent field studies[1, 2]. Both monomer density profiles, end-monomer distributions show that increasing linear chain length has a dramatic effect on the structure of brush, i.e. the relative position of star and linear chains intriguingly exchanges. Particularly, just slightly increasing linear chain induces a transition of linear conformation from collapsed to stretched. Similar effect is observed when increasing grafting density in the intermediate linear chain regime. At low grafting density, linear chains retract to the bottom of brush, meanwhile, stars domain in the upper layer of brush. With increasing grafting density, a certain fraction of linear chains squeeze out. At high grafting density, Most linear chains are stretched to the surface of brush. Our findings are summarized in the phase diagram. Further on, we studied these mixed binary brush that are immersed in changing quality solvent (from good solvent to poor solvent) by decreasing temperature. We can see that the composition in the periphery part of binary brush with intermediate linear chain length and grafting density transits from the mixture of free ends of linear chains and stars to free ends of stars. The quantity of these latter effects are insufficient to build switchable systems. However, it gives a hint that modifying the chemical properties of different spices to obtain solvent selectivity will be helpful to build a smart environment-responsive coating.

Results and perspective of the future work are summarized in the last chapter.

Key Words: θ-solvent, starlike polymer brushes, mixed polymer brushes, Molecular Dynamics, Mean-Field theory

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